

PATENT SPECIFICATION

DRAWINGS ATTACHED

893,524



Date of Application and filing Complete Specification Aug. 19, 1959.

No. 28410/59.

Application made in Hungary on Aug. 22, 1958.

Complete Specification Published April 11, 1962.

Index at acceptance:—Class 2(3), C3A5(C1A2:E:F4A), C3A13A3(A1C:B1:D:J1).

International Classification:—C07b.

COMPLETE SPECIFICATION

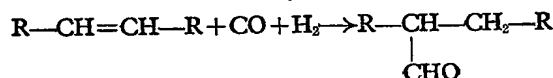
Method of Removing Dissolved Cobalt Compounds from the Products of Cobalt-catalysed Reactions

We, MAGYAR ASVANYOLAJ ES FOLDGAZ KISERLETI INTÉZET, of Wartha Vince utca 2—6, Veszprem, Hungary, a body corporate organised under the Laws of Hungary, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

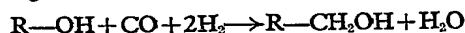
10 This invention relates to a method of removing dissolved cobalt compounds from the

products of cobalt-catalysed synthesis performed with carbon monoxide and of re-using said compounds for catalysing the synthesis.

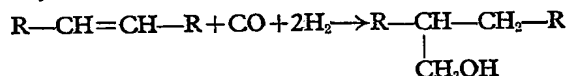
Diverse organic syntheses performed with carbon monoxide are catalysed by metallic cobalt or a cobalt compound. Such processes include for instance the so-called oxo-synthesis:—



the synthesis of homologue alcohols:—



and the direct alcohol synthesis:—



In all these syntheses the reaction is catalysed by complex compounds of cobalt with carbon monoxide, namely by cobalt carbonyls, which are either formed during the principal reaction from the cobalt metal or compound introduced into the synthesis reactor, or which are introduced into the reactor directly in the form of carbonyls.

These cobalt carbonyls are readily soluble in organic liquids, i.e. in hydrocarbons, aldehydes, alcohols, and therefore leave the reactor dissolved in the synthesis products. Consequently this escaping cobalt must be continuously replaced and at the same time the cobalt which is dissolved in the reaction products in the form of the cobalt carbonyls and other cobalt compounds must be removed: as it would otherwise considerably interfere with the further processing of the reaction products, especially with the recovery therefrom of the valuable constituents.

[Price 4s. 6d.]

Known methods of decobaltifying the synthesis products have the disadvantage that the cobalt compounds which are dissolved in the product are chemically reacted in a manner that also affects the valuable primary products and reduces this yield.

It has already been proposed to drive the valuable product out of the reaction mixture by careful distillation and to prevent decomposition of the $CO_2(CO)_8$ which remains in the distillation residue by the application of carbon monoxide pressure. However, since some of the cobalt compounds are volatile this method is applicable only to readily volatile synthesis products.

Experiments performed by us have adduced the surprising result that cobalt can be removed from the reaction product of cobalt-catalysed syntheses performed with gas mixtures containing carbon monoxide and hydrogen by passing a gas mixture of CO and H_2

- through the cobalt-containing synthesis product at a temperature between 140 and 240° C. and with a H₂ partial pressure of at least 10 atmospheres, and with a CO partial pressure so chosen above 10 atmospheres as to be higher than the decomposition pressure of the cobalt compounds at the temperature employed. We have found that the cobalt compounds dissolved in the synthesis product will behave in these circumstances like a liquid boiling at 80° C. Indeed, practically all of the cobalt content of the synthesis product volatilizes and is carried off by the gases emerging from the liquid synthesis product. The removal of the cobalt can thus be performed in similar conditions as the synthesis reaction itself so that the possibility of the concurrence of undesirable side reactions with the decobaltification process is reduced to a minimum.
- In the method according to the invention, as distinct from known methods, the cobalt does not therefore remain in the residue but appears in the emerging gases as a readily volatile component, the cobalt content of the residue gradually diminishing. It is essential that CO and H₂ are simultaneously present in the gases which are passed through the cobalt-containing synthesis product since the cobalt will remain in the residue if only carbon monoxide is passed through the product.
- We are aware of the process described and claimed in the United Kingdom Patent Specification No. 667,824, in which oxygen-containing organic compounds obtained by the action of carbon monoxide, with or without hydrogen, on various organic compounds in the presence of catalysts which produce soluble metal compounds in the final product, are treated at elevated pressure and temperature with a gas containing, besides hydrogen, carbon monoxide in such a quantity from 0.1 to 50% that reduction of the oxygen-containing compounds is checked, but the metal compounds dissolved in the product are decomposed to the metallic elements. Such a decomposition, cannot, however, take place but on the condition that the decomposition pressure of the metal carbonyl compounds is, at the elevated temperature employed, well above the CO partial pressure, as stated also in said specification, in contradistinction to one of the main features of our invention according to which the CO partial pressure is always higher than the decomposition pressure of the cobalt carbonyls at the temperature employed so as to prevent the decomposition of the dissolved cobalt compounds to metallic cobalt and recover the cobalt in the form of carbonyls which being readily soluble in the crude stock for the synthesis reaction are best adapted for re-use as catalysts in this reaction.
- The process of removing the cobalt according to the invention may be performed in any pressure-tight vessel suitable for the maintenance therein of the required temperature. Conveniently a vessel similar to the reactors which are conventionally used in high pressure processes may be employed.
- The gas mixture which is blown through the product may contain minor quantities of inert gases such as N₂, CH₄, CO₂ as impurities. These will affect the performance of the manner in which the process is conducted only insofar as the total pressure must be increased in order to establish the necessary CO and H₂ partial pressures. Water gas (CO:H₂=1:1) produced in conventional manner or the known synthesis gas (CO:H₂=1:2) have been found to be especially suitable mixtures. However, other gas mixtures rich in CO may likewise be used.
- Blowing of the gas mixture through the synthesis product is continued until the cobalt content of the latter has reached the desired low level. The time required to achieve this result depends upon temperature and the volume of gas blown through the product per unit of time.
- The cobalt contained in the form of gaseous cobalt compounds in the emerging gases can be removed in any known manner and after having been freed of cobalt the gas mixture can be returned to the reactor in which the synthesis product is decobaltified.
- However, if the synthesis products that are to be decobaltified according to the invention consist substantially of components boiling between 80 and 250° C., then according to another feature of the invention the cobalt compounds can be most readily removed from the emerging gases, without the concurrence of chemical reactions, in the form of a liquid which contains more cobalt than the undecobaltified synthesis product and which can therefore be directly returned as catalyst solution to the synthesis reaction. The said cobalt-containing liquid is separated, according to the invention, by cooling the emerging gases to a temperature between 0 and 60° C. under an H₂ partial pressure of at least 10 ats., preferably between 30 and 400 ats., and under a CO partial pressure above 10 ats., preferably between 30 and 400 ats. The resultant condensate can be recycled and used as catalyst solution in the synthesis reaction, even after it has been stored, because the compounds contained therein are not significantly reactive with cobalt carbonyls. The components of the emerging gases which remain in the gaseous state after cooling can be returned to the decobaltification reactor since they constitute a CO and H₂ mixture which is now poor in cobalt.
- In order to obtain a condensate from the gases emerging from the decobaltification reactor, which is suitable as a catalyst solution and which is much richer in cobalt than the synthesis product the gases emerging from the decobaltification reactor before being

cooled can be contacted in counter-current with a recycled portion of the condensate obtained by cooling, and thus further enriched with cobalt. This counter-current contact is conveniently effected in an extension of the decobaltifying reactor and the recycled proportion of the condensate may be between 10 and 90%, conveniently between 20 and 75% of the quantity that can be condensed by cooling the gases to between 0 and 60° C.

A number of illustrative examples of the invention will now be described by reference to the accompanying drawings.

Fig. 1 is a form of construction of decobaltification apparatus which is both continuously and discontinuously operable. In discontinuous operation the decobaltification reactor 2 which may have a packing of solid material, or the usual trays to improve gas distribution, is filled with the cobalt-containing reaction product of the synthesis process. The pressure is then raised to the required pressure by a blower P_1 which supplies the same gas mixture that is to be blown through the product, and the temperature is raised to the desired level. The gas cycle is then switched on by starting up blower P_2 . The gases emerging overhead from reactor 2 are cooled in a cooler 13 and separated from the condensed cobalt-containing liquid in the pressurised separator 14. The liquid collects in separator 14, whereas the gas mixture which is now poor in cobalt is returned to the bottom of reactor 2. Circulation is thus continued until the cobalt content of the synthesis product in reactor 2 has dropped to the desired low level which can be checked by taking samples from valve 3. When the gas circulation has been stopped the decobaltified product can be withdrawn through valve 4, whereas the condensate containing cobalt carbonyl is drained through valve 15.

If operation is continuous the synthesis product which is to be decobaltified is continuously admitted into reactor 2 through valve 1 and the decobaltified product is continuously withdrawn through valve 4. The cobalt-containing liquid collecting in separator 14 may likewise be continuously drained through valve 15.

Fig. 2 illustrates the manner in which the cobalt cycle shown in Fig. 1 can be connected with the synthesis plant in a case in which the continuously performed synthesis and the decobaltification of the synthesis product require separate gas circulations.

The synthesis reactor 10 is supplied by means of a pump P_4 with the liquid crude stock, by a blower P_5 with the gas mixture required for performing the synthesis, by a blower P_6 with a recycled gas mixture, and by a pump P_8 with the cobalt carbonyl-containing condensate from a separator 14. From the synthesis reactor 10 the mixture of final gases and of the reaction product is taken to

a separator 11 from which the gas mixture that is to be recycled into the synthesis reactor is withdrawn by blower P_6 , whereas the cobalt-containing liquid product flows overhead into the decobaltifying reactor 2 through which the decobaltifying gas mixture of CO and H_2 is blown by blower P_2 in constant circulation from the bottom upwards in counter-current to the liquid for stripping the volatile cobalt compounds therefrom. The decobaltified synthesis product is withdrawn from the bottom of reactor 2. The cobalt-containing gas emerging overhead is cooled in cooler 13 and the cobalt-containing condensate is separated in separator 14 from the remaining gas which is now again poor in cobalt. The gas return by blower P_2 into the decobaltifying reactor 2 and the losses of decobaltifying gas which arise in course of the cycle are made good by blower P_1 . The cobalt-containing condensate is recycled to the synthesis reactor 10 to serve as catalyst solution, it being conveyed partly by pump P_8 directly and partly through a collecting tank 16 by a pump P_9 . The purpose of the collecting tank is to ensure a uniform supply of catalyst solution to the synthesis reactor, surplus being stored in the tank for replacement of any deficiency in the reactor that may arise.

If synthesis and decobaltification can be performed with a gas mixture of the same composition the plant described with reference to Fig. 2 may be simplified in the manner illustrated in Fig. 3. In this installation blower P_1 performs the functions of the two blowers P_1 and P_5 in Fig. 2, and the distribution of the fresh gases supplied by blower P_1 and of the decobaltified gases recirculated from separator 14 by blower P_2 , between the synthesis reactor 10 and the decobaltification reactor 2 is controlled by valve 12. Separator 11 and blower P_6 in Fig. 2 are likewise redundant because, on the one hand, the gases which do not participate in the synthesis reaction need not be separated from the liquid admitted to the decobaltification reactor 2 and, on the other, the same gases can be recycled together with the decobaltification gases.

EXAMPLE 1

In an installation according to Fig. 3 a cracked petroleum product containing 20% olefines and boiling between 190 and 220° C. and a gas mixture containing CO and H_2 in the proportion by volume of 2:1 were used for performing a direct alcohol synthesis at 210° C. and at a pressure of 300 ats in a reactor 10.

Pump P_4 supplied the synthesis reactor 10 which had a capacity of 12.6 litres with 1000 g per hour of liquid crude stock in which 5 g of cobalt stearate per kg crude stock had been dissolved, and 1 stand. cub. m/h of the gas mixture maintained in circulation by blower

P₂ were branched off into the synthesis reactor. 1050 g of synthesis product of the following composition emerged from the reactor 10 per hour:—

	% by weight
C ₁₃ aldehyde - - - - -	1.2
C ₁₃ alcohol - - - - -	27.3
high boiling by-products - - -	3.4
10 hydrocarbons - - - - -	67.8
cobalt (in solution) - - - - -	0.30

This product was taken to a decobaltification reactor 2 which was 3.2 metres long and had a diameter of 65 mm and 10 trays with bubble caps. Decobaltification was performed at 200° C. and at a pressure of 300 ats. with the same gas mixture as that used in the synthesis reaction. Per hour 6 stand. cub. m. of gas mixture were blown through the decobaltification reactor 2 via control valve 12. The product obtained at the bottom of the reactor contained less than 0.03% cobalt.

The cobalt-containing gases emerging from the decobaltification reactor overhead were cooled in cooler 13 to 15° C. and the condensate containing the cobalt carbonyls was separated in separator 14 from the cooled gas mixture which was now poor in cobalt. The gases were returned by blower P₂ to the synthesis cycle and through valve 12 into the decobaltification reactor. The volume of gas consumed by the synthesis was replaced through blower P₁. The latter introduced 0.3 stand. cub. m. per hour of a gas mixture containing 40% CO and 60% H₂ by volume.

The condensate containing the cobalt carbonyls, which had a content of 2.2% cobalt in solution, was fed back to the synthesis reactor by pump P₃ in suitable quantities to maintain the cobalt content of the reaction mixture at 0.3% based on the total weight of liquid.

In view of the fluctuations that may occur during decobaltification the cobalt content of the condensate collecting in separator 14 may vary, so that a direct return of the condensate would upset a uniform course of the synthesis reaction. Consequently the synthesis was at first performed exclusively with cobalt stearate and the resulting cobalt-containing condensate collected in tank 16. As soon as the cobalt content of the condensate was found to drop, pump P₆ was used to replace from tank 16 the quantity of cobalt required to maintain a uniform cobalt level in the synthesis reactor. On the other hand, an increase in the cobalt level inside the synthesis reactor consequent upon an excessive input of cobalt stearate with the crude stock could be prevented by draining part of the condensate from separator 14 into tank 16. In this manner a uniform cobalt level could be maintained in the synthesis reactor to ensure that the product obtained continued to of consequent composition.

Figs. 4 and 5 shows two alternative ways in which the condensate to be condensed in cooler 13 can be enriched with cobalt to ensure that the condensate returned as catalyst solution to the synthesis introduces a minimum of inert components.

In discontinuous operation of the decobaltification apparatus shown in Fig. 4, the reactor 2 is filled through valve 1 with cobalt-containing synthesis product, then the pressure in the system is raised to the desired level by means of blower P₁ introducing the CO+H₂ gas mixture, and as soon as the required temperature has been established the gas circulation is started by switching on blower P₂. The gas mixture blown through the decobaltification reactor strips the volatile cobalt carbonyls and passes through an enrichment zone 17 in counter-current flow to the condensate which has been condensed in a preliminary cooler 18 by moderate cooling, for instance to between 120 and 220° C., and which trickles through zone 17. The volume of this condensate is controlled by adjusting the temperature of the preliminary cooler 18 in such a way the cobalt concentration in the condensate collected in cooler 13 will reach the desired level. Due to this counter-current contact the gases emerge from zone 17 with an increased cobalt content and they are then cooled in cooler 13 to a temperature between 0 and 60° C. The resultant condensate which has a high cobalt content is collected in separator 14 and the remaining gas mixture which is now poor in cobalt is returned to the decobaltification reactor 2 by blower P₂. The composition of the circulating gas may be controlled by the introduction of fresh gas through blower P₁ and/or by blowing off gas through valve 9. Gas circulation is continued until a liquid sample tapped from valve 3 discloses the desired low cobalt content. The decobaltified final product is then withdrawn through valve 4.

In the apparatus shown in Fig. 5 the gas mixture leaving the enrichment zone 17 is taken directly to cooler 13 and is at once cooled to between 0 and 60° C., the proportion of the condensate collecting in tank 14 which is returned to zone 17 being adjusted by valve 19 until the condensate withdrawn through valve 15 is found to have the desired relatively high cobalt content.

Both the described methods of enriching the condensate with cobalt may also be continuously performed by introducing the synthesis product which is to be decobaltified continuously through valve 1 and withdrawing it through valve 4, whereas the cobalt-enriched condensate is likewise withdrawn continuously through valve 15. In this case it may be advisable to pack the decobaltifica-

tion reactor with solids or to provide it with trays.

Decobaltification as performed in the apparatus shown in Figs. 4 and 5 can be combined with the synthesis process in the same way as described with reference to Figs. 2 and 3.

EXAMPLE 2

A cracked petrol boiling between 90 and 100° C. and containing 20% olefines was used for a continuous direct synthesis of alcohol, and the synthesis product was continuously decobaltified in the manner illustrated in Fig. 4.

The synthesis was performed in three reactors, operationally connected in series, at a temperature of 210° C. and a pressure of 300 ats. with a gas mixture consisting of CO and H₂ in the proportion of 2:1 by volume. The catalyst was the condensate obtained from separator 14, a cobalt complex solution in petrol containing 2.5% cobalt. In order to replace the cobalt losses cobalt stearate was dissolved in the crude stock in proportions corresponding with a cobalt content of 0.03% by weight.

The reactors had a total volumetric capacity of 45 litres and 4 kg of crude stock, 0.85 kg of recycled cobalt solution, and 1.3 standard cub. m. of the gas mixture were introduced per hour.

The product obtained from the synthesis reactors amounted to 5.05 kg/h and had the following compositions:—

	% by weight
C ₃ alcohol - - - - -	16.5
C ₃ aldehyde - - - - -	1.6
hydrocarbons - - - - -	78.4
high-boiling by-products - -	2.5
cobalt compounds - - - - -	1.0

This product which had a net cobalt content of 0.41% was admitted at a temperature of 200° C. through valve 1 into a decobaltification and cobalt-enriching reactor provided in the lower decobaltification zone 2, which was 5 metres high, with twenty bubble cap trays, whereas the upper enrichment zone 17, which was 1.8 metres high, had six bubble cap trays. At an overall pressure of 300 ats., 8 stand. cub. metres per hour of a gas mixture of CO:H₂=2:1 by volume was passed through this reactor 2, 17. In the preliminary cooler 18 the gases were cooled sufficiently to condense 2.55 kg/h. This condensate was returned at condensing temperature to the top tray in the enrichment zone 17, whereas the gases escaping from cooler 13 were cooled to 20° C. In the separator 14 a condensate containing 2.5% cobalt was obtained at the rate of 0.85 kg/h. This was returned through valve 15 to the synthesis reactors as catalyst. The gases which did not condense in cooler 13 were returned by blower P₂ into the decobaltification reactor 2.

The decobaltified product withdrawn from the decobaltification reactor 2 through valve 4 mounted to 4.2 kg/h and had the following composition:—

	% by weight
C ₃ alcohol - - - - -	20.0
C ₃ aldehyde - - - - -	1.9
high-boiling by-products - -	3.1
hydrocarbons - - - - -	75.0

The final product had a cobalt content of 0.03% by weight.

EXAMPLE 3

In conjunction with a direct alcohol synthesis as described in Example 2 decobaltification of the synthesis product was performed at a temperature of 200° C. in apparatus according to Fig. 5.

The decobaltification zone 2 was constructed as in Example 2 and the same gas mixture was passed through the zone at the same rate and pressure as in Example 2. However, the enrichment zone 17, which had the same diameter, was 3 metres long and contained ten bubble cap trays.

3.4 kg petrol containing 2.5% cobalt were condensed in cooler 13 per hour. 0.85 kg/h of the condensate collecting in separator 14 were withdrawn through valve 15 and added to the crude stock (cracked petrol) as a catalyst, whereas the remainder of the condensate was returned to the top tray of the enrichment zone through valve 19.

The quantity and composition of the decobaltified final product withdrawn through valve 4 was in Example 2.

WHAT WE CLAIM IS:—

1. The method of removing dissolved cobalt compounds from the oxygen-containing products of cobalt-catalysed organic synthesis reactions performed with gas mixtures containing carbon monoxide and hydrogen, characterised in that a gas mixture of carbon monoxide and hydrogen is passed through the cobalt-containing synthesis product at a temperature between 140 and 200° C. and with a hydrogen partial pressure of at least 10 atmospheres, and with a carbon monoxide partial pressure so chosen above 10 atmospheres as to be higher than the decomposition pressure of the cobalt compounds at the temperature employed in which circumstances practically all of the cobalt content of the synthesis product volatilizes and is carried off by the gases emerging from the liquid synthesis product.

2. The method claimed in Claim 1 when applied to the decobaltification of synthesis products consisting substantially of components boiling between 80 and 250° C., in which the cobalt-containing stripping gases emerging from the liquid synthesis product subjected to decobaltification are cooled to a temperature between 0 and 60° C. under the partial pressures as specified in Claim 1

for the decobaltification of the synthesis product by stripping gases, and the condensate so obtained is recycled to the synthesis reaction to serve there as a catalyst.

5 3. The method claimed in Claim 2, comprising storing any condensate which may temporarily be in excess of the demand for catalyst solution in the synthesis reaction and introducing stored condensate into the synthesis reaction when the rate of condensation temporarily falls below the demand for catalyst solution in the synthesis reaction.

10 4. The method claimed in Claim 2 or 3, comprising contacting the emerging cobalt-containing stripping gases, prior to cooling the same, in countercurrent with a refluxed proportion of the condensate obtained by cooling the gases, for the purpose of enriching the stripping gases and thereby also the final condensate with cobalt.

15 5. The method claimed in Claim 4, wherein cooling of the emerging stripping gases to a temperature between 0 and 60° C. is performed in two stages and only the condensate
20 from the first cooling stage in which the gases are moderately cooled, for instance to between 120 and 220° C., is refluxed for contacting with the gases emerging from the liquid synthesis product.

6. The method claimed in Claim 4 or 5, wherein the refluxed condensate is contacted in countercurrent with the cobalt-containing stripping gases at the temperature and partial pressures as specified in Claim 1 for the decobaltification of the synthesis product by stripping gases.

7. The method claimed in any one or more of the preceding claims, in which decobaltification is continuously performed in direct conjunction with synthesis reactions continuously performed with a gas mixture of carbon monoxide and hydrogen, in such manner that the gas requirements of the synthesis reaction and of the decobaltification process are both supplied from a single common gas cycle.

8. The method of decobaltifying the oxygen-containing products of cobalt-catalysed organic synthesis reactions performed with gas mixtures containing carbon monoxide and hydrogen, substantially as herein described with reference to and as illustrated by any one of the accompanying drawings.

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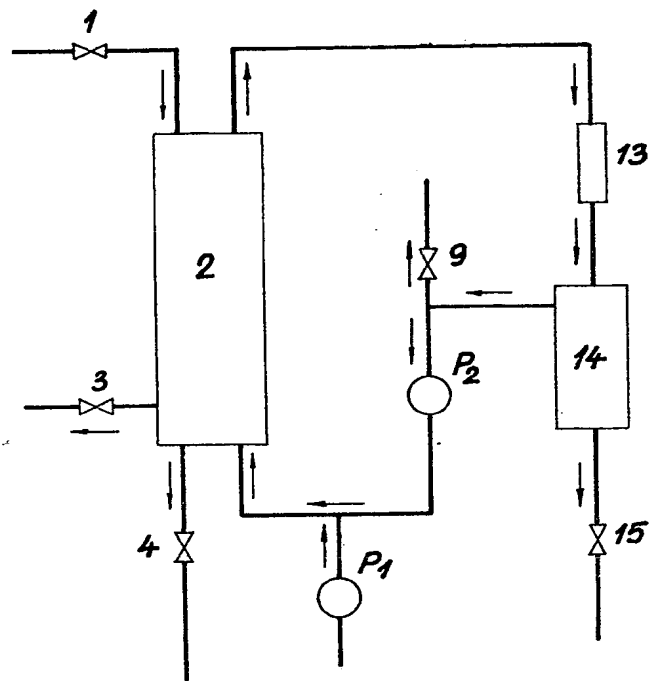


Fig. 1

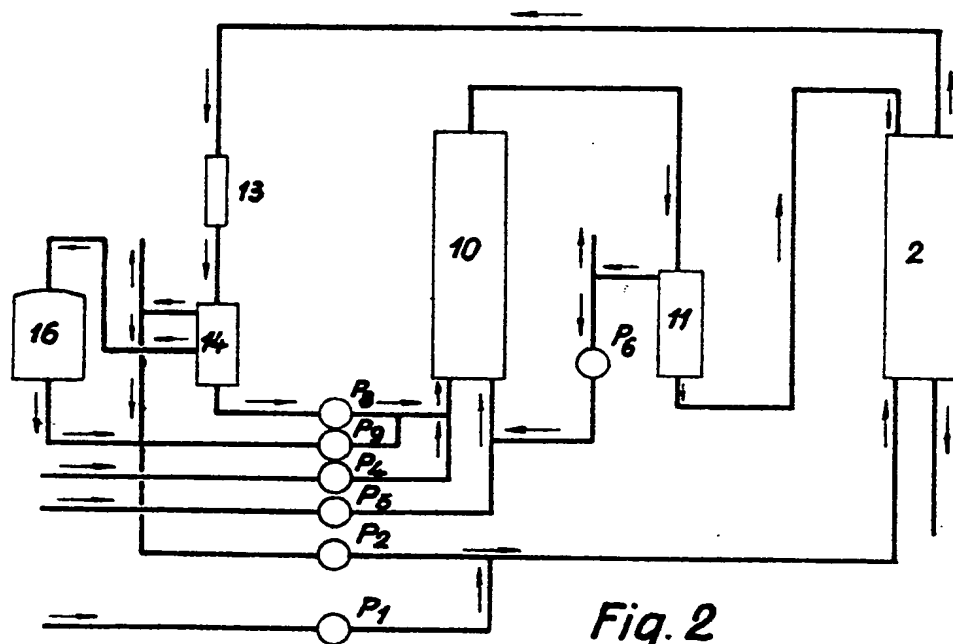


Fig. 2

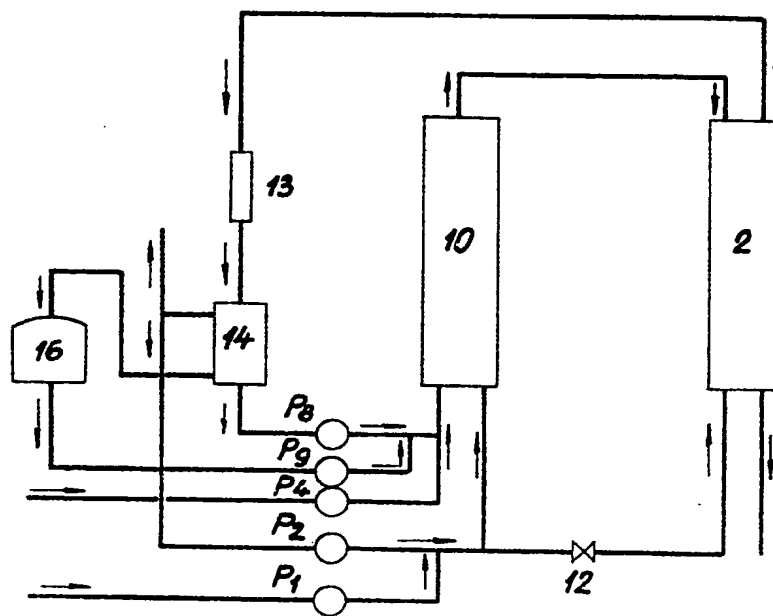


Fig. 3

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COMPLETE SPECIFICATION

3 SHEETS

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SHEETS 2 & 3

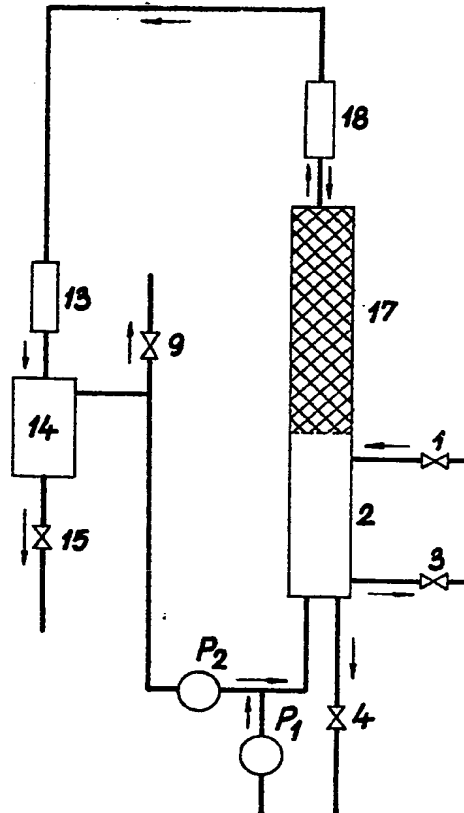
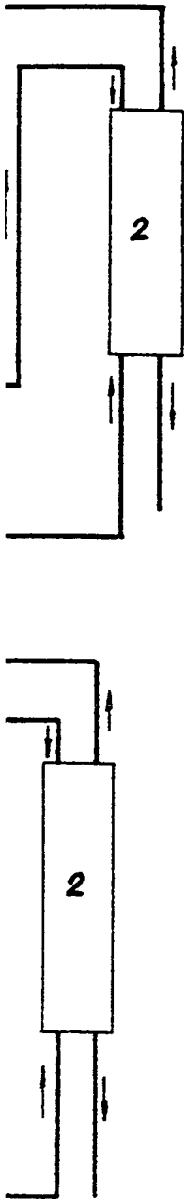


Fig. 4

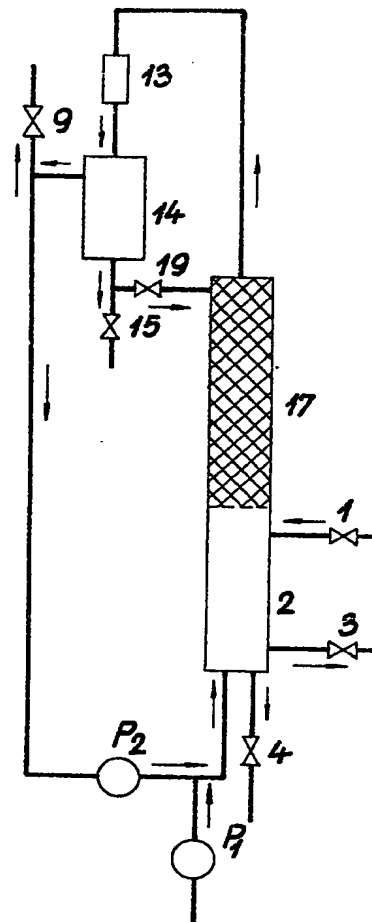


Fig. 5

